Reductive disproportionation of carbon dioxide by a Sm(II) complex: Unprecedented f-block element reactivity giving a carbonate complex†

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A macrocyclic organosamarium(II) complex has been shown to provide the first example of the reductive disproportionation of carbon dioxide, giving a bimetallic carbonate complex and carbon monoxide in a facile reaction under ambient conditions.

Synthetic strategies for the metal-mediated atmospheric capture of CO_2 remain a difficult challenge, despite this being nature's way of harnessing this vital commodity for living systems.[1] CO_2 is difficult to activate and/or reduce as it is a very inert substance, and is a tremendous thermodynamic sink in chemical synthesis design. The success of supercritical CO_2 as a solvent/extractant for a large range of efficient organometallic-based catalytic reactions is blatant recognition of its inertness with respect to many reactive species. Coordination (η^1-C and η^2-CO, as well as several bridging modes), reductive coupling (to oxalate), various stoichiometric and catalytic insertions, reductive deoxygenation (to CO and O^{2-}) and reductive disproportionation (to CO and CO_3^{2-}) or related O-transfer to other species have been established in the presence of transition metals.[2]
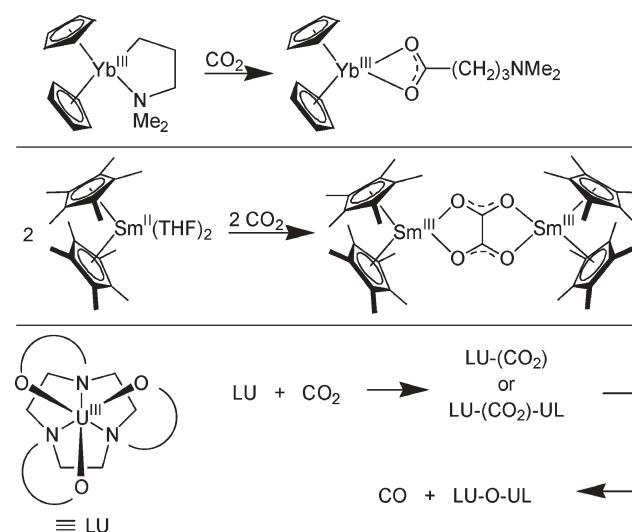
Structurally authenticated examples of the reactivity of f-block element organometallic complexes towards CO_2 have hitherto been limited to (i) insertions into Ln/Ac–C/X bonds (high/low oxidation state metals) giving carboxylates, carbamates and secondary products arising from their degradation,[3] (ii) reductive coupling by Ln(II) species to afford oxalates[4] and (iii) sterically crowded macrocyclic U(III) systems that give either η^1-O binding of $(CO_2)^-$ or further reduction leading to a bimetallic μ_2-O^{2-} complex and CO (via a spectroscopically observed bimetallic μ_2-CO_2 intermediate), depending on the steric bulk of the complex (Scheme 1).[5] There have also been non-crystallographically authenticated reports of reversible CO_2 binding to various Ln(III) reagents and their CO_2 insertion products.[6] Interesting reactivity towards CO_2 was reported for the crowded $[(C_5Me_5)_3Ln^{III}]$ complexes (Ln = Sm and Nd), which typically undergo Ln–C σ-bond insertions or ligand-based reductions.[7] The outcome was of the former's reactivity pattern giving $[(C_5Me_5)_2Sm^{III}(O_2CC_5Me_5)]$, and suggested to be linked to the weak reducing ability of $[(C_5Me_5)_3Sm^{III}]$ relative to $[(C_5Me_5)_2Sm^{II}]$.

Reductive disproportionation of CO_2 is a conspicuously absent precedent in low-valent f-block element chemistry, given that this was identified early in transition chemistry as a common outcome for electron-rich systems.[8] We report here the first example of CO_2 reduction via this reactivity type for an f-block element complex, leading to a carbonate complex and the concomitant formation of CO.

An excess of CO_2 was administered to a partially evacuated flask containing a purple toluene solution of the Sm(II) precursor[9] under argon, giving an orange solution within 30 minutes at room temperature, from which orange crystals of **1** were isolated in moderate yield (Scheme 2). Characterisation of **1** included ^1H and ^{13}C NMR spectroscopic analysis, X-ray crystal structure determination and microanalytical data.†‡

The solid state structure of **1** confirms its identity as a bimetallic carbonate complex having two fold crystallographic symmetry, with the O1–C39 bond of the carbonate lying on the two fold axis. The well-established η^5:η^1:η^5:η^1 macrocyclic binding mode is observed in the solid state structure of **1** (Fig. 1(a)). The Sm–N and Sm–centroid (Ct) distances to the η^1-bound pyrrolide and η^5-bound N-methyl pyrrolyl units are in accordance with previously reported Sm(III) complexes.[9] The sterically demanding macrocycle limits the carbonate coordination environment, which bridges the Sm centres in an μ_2:$\eta^2(O,O')$:$\eta^2(O,O')$-fashion. The Sm–O distances are disparate, with those to the bridging O-centre being the longer of the two. This binding mode leads to steric interactions between macrocycles, involving the *meso*-ethyl group and the 3,4-positions of the N-methyl pyrrol units, which induces a twist in the bimetallic species, reducing the overall symmetry to


Scheme 1 Examples of structurally authenticated reactivity patterns for carbon dioxide in f-block element organometallic chemistry.[3–5]

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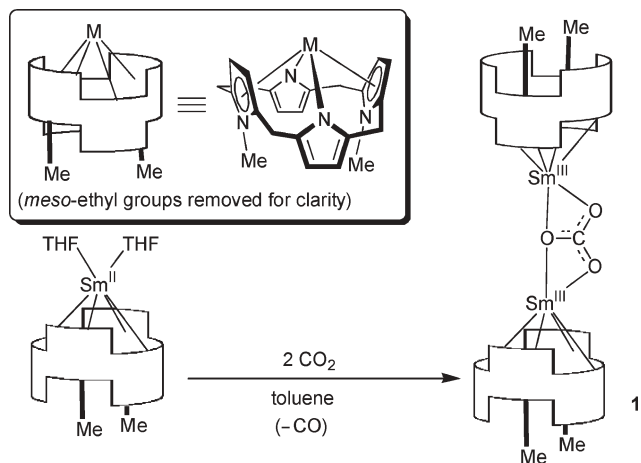
Scheme 2 Synthesis of the Sm(III) porphyrinogen carbonate **1**.

C_2 (Fig. 1(b)). The carbonate binding mode is the lowest hapticity to be observed in f-block element chemistry, and is known for only one other macrocyclic complex.[10] The carbonate ligand in **1** is accessible and potentially open to further reactivity, including removal or Lewis basic behaviour (Fig. 1(b)).

The ^1H NMR spectrum of **1** in C_6D_6 at room temperature indicates a fluxional process giving rise to effective C_{2v} macrocyclic symmetry (overall D_{2h} symmetry for the bimetallic structure). No signal coalescences are observed at low temperature (-60 °C in [D]$_8$-toluene) in the ^1H NMR spectrum. This is suggestive of the frailty of the long Sm–O bonds involving the bridging O-centre of the carbonate. The lability of these interactions (chelate ring opening) would allow rotation of the macrocyclic unit about the remaining Sm–O bond.[11] The ^{13}C NMR spectrum of **1** is consistent with this interpretation and displays a resonance at δ 190.9, assigned to the carbonate ligand.
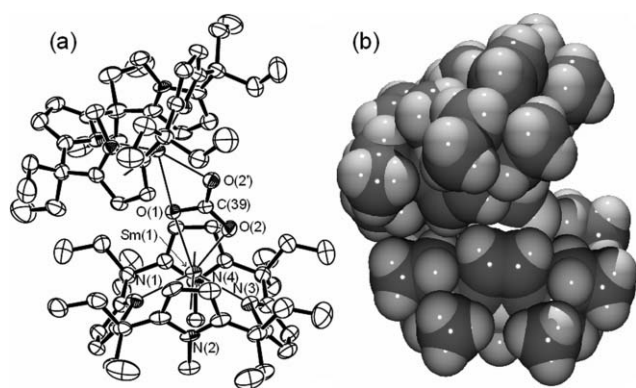

Fig. 1 Molecular structure of **1**. (a) General view with 50% probability ellipsoids. All hydrogens omitted for clarity. (b) Space-filling representation of the same view as (a), highlighting the congestion between the macrocycles and the accessibility of the carbonate. Selected distances (Å) and angles (°): Sm1–N1,N3 = 2.534(4), 2.483(4), Sm1–Ct2,Ct4 = 2.6$_4$, 2.6$_1$, Sm1–O1,O2 = 2.340(3), 2.580(1), C39–O1,O2 = 1.317(7), 1.276(4); N1–Sm1–N3 = 120.4(1), Ct2–Sm1–Ct4 = 163.5, N1–Sm1–O1,O2 = 101.2(1), 153.9(1), N3–Sm1–O1,O2 = 138.4(1), 85.3(1), O1–Sm1–O2 = 53.4(1), Sm1–O1–Sm1′ = 175.7(2), O2–C39–O1,O2′ = 117.8(3), 124.3(6). Prime (′) denotes symmetry equivalent atom generated by -x,y,3/2-z.

Reductive disproportionation of CO_2 has been established unequivocally *via* mass spectrometry as the synthetic pathway leading to carbonate formation in **1**.† Headspace sampling from the reaction vessel during the synthesis of **1** confirmed the presence of CO by high resolution GC-MS. GC conditions easily separated CO_2 from a mixed chromatographic peak containing CO, N_2 and O_2, the latter pair resulting from minor amounts of adventitious air. Complete mass resolution of CO (ion centroid at m/z 27.9948) from N_2 (28.0061) and O_2 (31.9898) was subsequently attained. CO contamination in the CO_2 was below detection limits and CO formation from CO_2 during analysis was ruled out.

We are tempted to attribute the prior lack of a well-characterised CO_2 reductive disproportionation product in f-block element chemistry simply to the continued scarcity of well-researched low-valent lanthanide and actinide systems. Differing steric limitations of ligand frameworks have already proved to be influential in uranium-based CO_2 reductions, and such effects may well also play a part in lanthanide-based chemistry. The non-participating ligands featuring in the CO_2 reduction product presented here, and those of Evans[4] and Meyer[5] based on cyclopentadienyl and multidentate macrocyclic ligands, all vary in steric influence/restriction for small molecule binding, and certainly there is much scope around these systems that allows for further investigations. For example, further ligand substituent size reduction in the macrocyclic system of Meyer may give rise to subsequent reactivity of the μ_2-O^{2-} species, resulting from deoxygenation, to give carbonate. What is the preferred CO_2 reduction product in less hindered uranium systems? Can such reactive low-valent precursors be prepared in order to test this? Similarly, can CO_2 reduction products, other than coupling to oxalate, be observed in bulkier lanthanocenes? In this regard, we note the established feature of the macrocycle studied here as being (in some regards at least) more sterically demanding than the bis(pentamethylcyclopentadienyl) ligand set (*viz*, the structural differences recently established for the monomeric and trimeric structures of $Sm^{III}Me$ derivatives[12]). The carbonate formation presented here could be the result of the destabilisation of an initially formed oxalate complex that is prevented from binding with the seemingly preferred "side-on" η^2 binding mode[13] due to the narrow, short binding groove, which may limit oxalate binding to "end-on" or carboxylate type η^2-binding.

In conclusion, we have identified the first example of the reductive disproportionation of carbon dioxide by an f-block element complex. This has completed the array of reaction pathways known for transition metal-mediated CO_2 reductions. The result highlights potential shortcomings in understanding the preferred products in f-block element CO_2 reduction *vs.* outcomes that result from steric limitations. We are continuing to study the reactivity of the reported complex and are attempting to establish the primary product in its formation (possibly *via* a reductive deoxygenation intermediate or oxalate decomposition). In the broader sense, we are widening our studies into small molecule reduction processes with macrocycle-bound f-block metals, as our recent studies have shown unique outcomes.

Notes and references

‡ *Synthesis of* **1**. To a stirred toluene solution (80 mL) of the Sm(II) precursor[9] (0.86 g, 1.00 mmol), an excess of dry carbon dioxide (over P_2O_5) was introduced into the reaction vessel. The colour of the solution changed from purple to light orange, and a pale yellow solid formed over 30 min. The solution was filtered, the toluene removed *in vacuo* and the orange product extracted into a warmed THF solution. Filtration and concentration *in vacuo* gave a crystalline orange product upon standing overnight (0.40 g, 54%). Found: C, 62.05; H, 7.5; N, 7.7. $C_{77}H_{108}N_8O_3Sm_2$ requires: C, 61.9; H, 7.3; N, 7.5%. δ_H(300 MHz, C_6D_6, 298 K): −0.51 (24 H, m, CH_3), 1.09 (12 H, s, NCH_3), 1.22 (8 H, m, CH_2), 2.13 (8 H, m, CH_2), 2.26 (8 H, m, CH_2), 2.43 (8 H, s, =CH, pyrMe), 3.57 (24 H, m, CH_3), 6.14 (8 H, m, CH_2) and 6.79 (8 H, s, =CH, pyr). δ_C(75.4 MHz, C_6D_6, 298 K): 7.5, 10.4 (CH_3), 21.0, 33.9 (CH_2), 31.6 (CH_3), 47.3 (C), 97.0 (=CH, pyrMe), 101.3 (=CH, pyr), 133.8 (=CR, pyrMe), 154.6 (=CR, pyr) and 190.8 (C, CO_3).

Crystal data for **1**: $C_{77}H_{108}N_8O_3Sm_2 \cdot 2(C_4H_8O)$, $M = 1782.83$, monoclinic, space group $C2/c$ (no. 15), $a = 16.838(7)$, $b = 22.858(3)$, $c = 22.177(1)$ Å, $\beta = 95.27(4)°$, $V = 8500(6)$ Å^3, $Z = 4$, $\mu = 1.43$ mm^{-1}, Enraf-Nonius CAD4 diffractometer, $T = 193$ K, λ(Mo-Kα) = 0.71073 Å, 7640 reflections measured, 7430 independent ($R_{int} = 0.025$), $5790 > 4\sigma(F)$, $R = 0.040$ ($F > 4\sigma(F)$), $R_w = 0.120$ (all data). The structure was solved by direct methods, and all non-hydrogen atoms were subsequently refined anisotropically with hydrogens included in calculated positions using a riding model. Two THF solvent molecules were located in the asymmetric unit. One THF is well defined. The second is disordered across a crystallographic two-fold symmetry axis, such that two ring atoms lie on the rotation axis (modelled with five anisotropic carbon atoms without hydrogens included). The structure was solved and refined using SHELXS-97 and SHELXL-97, and visualised using X-SEED.[14] CCDC 617956. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611784h

1 G. Parkin, *Chem. Rev.*, 2004, **104**, 699.
2 For reviews, see: D. H. Gibson, *Chem. Rev.*, 1996, **96**, 2063; W. Leitner, *Coord. Chem. Rev.*, 1996, **153**, 257; X. Ling and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27.
3 For examples, see: (*a*) H. Schumann, J. Meese-Marktscheffel, A. Dietrch and H. Görlitz, *J. Organomet. Chem.*, 1992, **430**, 299; (*b*) Y. F. Rad'kov, E. A. Fedorova, S. Y. Khorshev, G. S. Kalinina, M. N. Bochkarev and G. A. Razuvaev, *Russ. J. Gen. Chem.*, 1986, **56**, 336; (*c*) W. J. Evans, K. A. Miller and J. W. Ziller, *Inorg. Chem.*, 2006, **45**, 424; (*d*) U. Baisch, D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti and A. Merigo, *Eur. J. Inorg. Chem.*, 2004, 1219.
4 W. J. Evans, C. A. Seibel and J. W. Ziller, *Inorg. Chem.*, 1998, **37**, 770; W. J. Evans, J. M. Perotti, J. C. Brady and J. W. Ziller, *J. Am. Chem. Soc.*, 2003, **125**, 5204.
5 I. Castro-Rodríguez and K. Meyer, *Chem. Commun.*, 2006, 1354 and references therein.
6 M. N. Bochkarev, E. A. Fedorova, Y. F. Radkov, S. Y. Khorshev, G. S. Kalinina and G. A. Razuvaev, *J. Organomet. Chem.*, 1983, **258**, C29.
7 W. J. Evans, J. M. Perotti, S. A. Kozimor, T. M. Champage, B. L. Davis, G. W. Nyce, C. H. Fujimoto, R. D. Clark, M. A. Johnston and J. W. Ziller, *Organometallics*, 2005, **24**, 3916.
8 Carbonate formation has been reported as a tertiary process arising from CO_2 reaction with degradation products following initial CO_2 insertions, though no experimental or characterisation data has appeared (ref. 3a). A very recent report has shown that thermolysis (650 °C) of CO_2 insertion products leads to carbonate formation: U. Baisch, S. Pagano, M. Zeuner and W. Schnick, *Eur. J. Inorg. Chem.*, 2006, 3517. A report exists of carbonate complex formation by CO_2 reduction with a Sm(II) complex, but no characterisation of co-formed carbon monoxide was offered: W. J. Evans, presented, in part, at *PacifiChem 2005*, Abstract INOR-745, Honolulu, December, 2005.
9 J. Wang, A. K. J. Dick, M. G. Gardiner, B. F. Yates, E. J. Peacock, B. W. Skelton and A. H. White, *Eur. J. Inorg. Chem.*, 2004, 1992.
10 G. Bombieri, F. Benetollo, A. Polo, K. K. Fonda and L. M. Vallarino, *Polyhedron*, 1991, **10**, 1385.
11 This process likely represents the minimum fluxionality that can account for the solution behaviour of **1**. More extensive fluxional processes cannot be ruled out without further investigations. Rotation of the macrocyclic units about intact Sm–O–C–O chelate rings could also account for the appearance of the room temperature ^{1}H NMR spectrum of **1**, but this is not likely given the narrow binding groove available for auxiliary ligands that the macrocycle offers.
12 J. Wang, M. G. Gardiner, B. W. Skelton and A. H. White, *Organometallics*, 2005, **24**, 815; W. J. Evans, J. M. Perotti and J. W. Ziller, *J. Am. Chem. Soc.*, 2005, **127**, 3894.
13 Many binding modes for oxalate are known in f-block element chemistry. The binding mode referred to forms at least a component of the binding type in all cases, except for $[NH_4]_4[U(C_2O_4)_3(O)_2]$, which features one of the three oxalates bound "end-on η^2-*O*,*O*'": N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1973, 1610.
14 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997; L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.